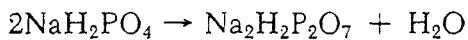


soda ash to yield a DSP solution, which may be dried to give anhydrous Na_2HPO_4 or crystallized to give $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$. These compounds are calcined at a high temperature in an oil- or gas-fired rotary kiln to yield TSPP in a plant such as that shown in Fig. 1.8. The reactions may be written:



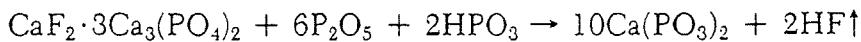
A nonhygroscopic sodium acid pyrophosphate is used extensively as a chemical leavening agent in making doughnuts, cakes, and packaged biscuit doughs. It is manufactured by partially dehydrating monosodium acid orthophosphate at a temperature of 160°C over the course of 6 to 12 h.



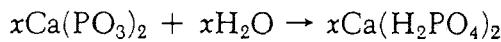
CALCIUM PHOSPHATES. Monobasic calcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] is manufactured by crystallization, after evaporation and some cooling of a hot solution of lime and strong furnace phosphoric acid. The crystals are centrifuged, and the highly acidic mother liquor returned for reuse. This acid salt is also made by spray-drying a slurry of the reaction product of lime and phosphoric acid. This product is used for baking powder.

Dibasic Calcium Phosphate. Dibasic calcium phosphate, which is used as a polishing agent in dentrifices, is manufactured from furnace-grade phosphoric acid and lime.

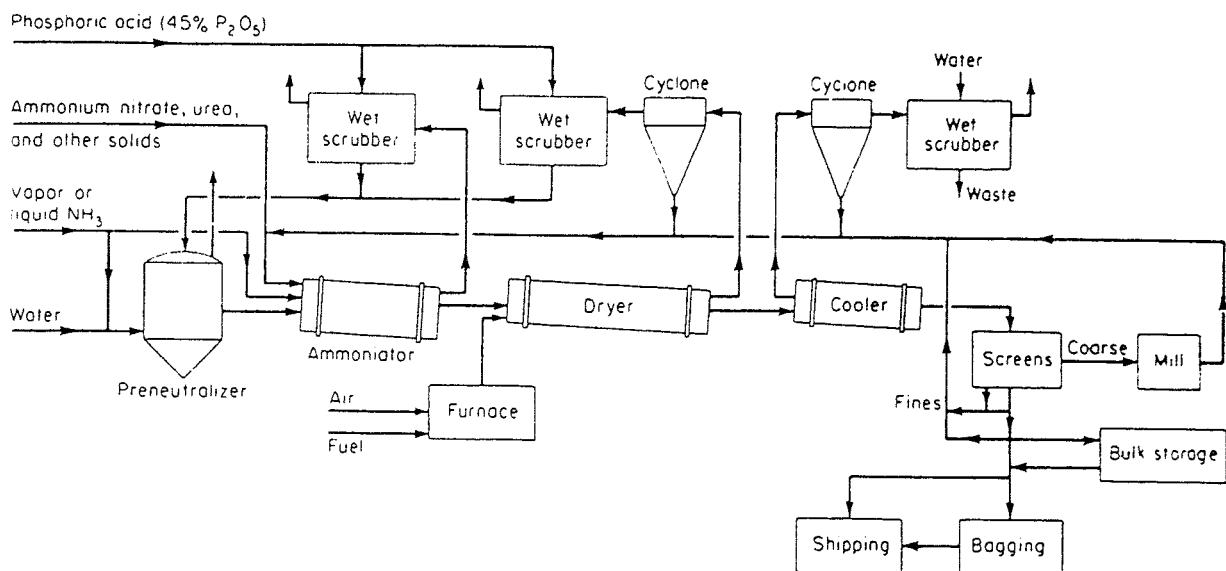
Calcium Metaphosphate. In 1937, the TVA developed a concentrated fertilizer, $\text{Ca}(\text{PO}_3)_2$, from phosphate rock by the following reaction:



In this process the P_2O_5 contacts the lump rock in a vertical shaft. About 20,000 t of phosphorus equivalent has been manufactured per year. This calcium metaphosphate may be regarded as a dehydrated triple superphosphate made directly from phosphate rock. The calcium metaphosphate is quite insoluble, and it must hydrolyze to become effective:



GRANULAR HIGH-ANALYSIS FERTILIZER. This is basically a commercial adaptation of the TVA process (Fig. 1.9), designed for the manufacture of diammonium phosphate fertilizer (DAP), either 21-54-0, using furnace phosphoric acid, or 18-46-0, with wet-process phosphoric acid or for any of many grades of granular fertilizer (cf. Chap. 26). The last-mentioned requires the addition of facilities for metering solid raw materials and sulfuric acid to the ammoniator. Vapor or liquid anhydrous ammonia and phosphoric acid (40 to 45% P_2O_5) are metered continuously to an agitated atmospheric tank (pneumatic neutralizer) in proportions to maintain a ratio of 1.3 to 1.5 mol of ammonia per mole of phosphoric acid. This ratio is the optimum for maintaining fluidity of the slurry with a minimum quantity of water and a reasonable ammonia loss in the exit vapor from the pneumatic neutralizer. In the pneumatic neutralizer the heat of reaction elevates the temperature of the mass, evaporating approximately 100 kg of water per metric ton of product. The slurry formed in the pneumatic neutralizer flows into a TVA-type ammoniator-granulator at about 120°C, where it is distributed evenly over the bed of



In order to produce 1 t, grade 18-46-0 DAP, the following materials and utilities are needed:

Ammonia	220 kg	Fuel	525 MJ
Phosphoric acid	465 kg	Direct labor	0.5 work-h
Electricity	200 MJ _e		

Fig. 1.9. Flowchart for the manufacture of diammonium phosphate (DAP) or high analysis fertilizer. (Austin Co.)

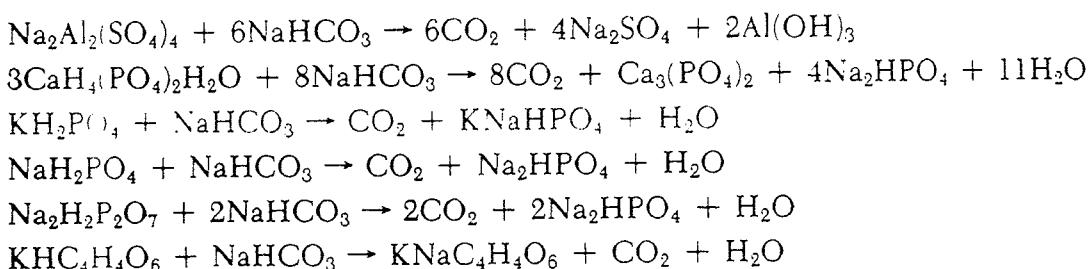
solid material and, for most grades, reacts with additional ammonia fed through a distributor pipe below the surface of the bed to complete the reaction with a molar ratio of 2.0 (diammonium phosphate).¹⁸ Dried recycle material from product screening is used to control the moisture, and additional solid raw materials are metered into the ammoniator, depending on the grade of fertilizer in production. The ammoniator combines the functions of chemical reaction, mixing, and formation of the proper size and shape of granular particles. The moist granules leaving the ammoniator fall into an oil- or gas-fired cocurrent rotary dryer, where the moisture content of the material is reduced to about 1%. The dry product is then cooled by a countercurrent flow of air in a rotary cooler and screened, the coarse material being milled and returned to the ammoniator-granulator. In some plants the cooler is eliminated, and hot screening is used. The fines and, if necessary, some of the product are recycled to the ammoniator to control granule formation and size. The product is conveyed to bulk storage or bagged. The exhaust gases from the dryer and cooler pass through cyclones or a wet scrubber for dust recovery. Exhaust gases from the ammoniator are scrubbed with the incoming phosphoric acid, and in some plants the phosphoric acid stream is split, a portion being used to scrub the vapor from the rotary dryer to minimize ammonia loss.

BAKING POWDERS

The baking-powder industry is an important but indirect consumer of phosphate rock. Use of leavening agents to produce aeration and lightness in breads and cakes has been¹ since the time of the Egyptians and was handed down by the Greeks and Romans. Le

¹⁸Chopey, DAP: New Plant Ushers in Process Refinements, *Chem. Eng.* 69 (6) 148 (1962); Pipe Reactor Making Diammonium Phosphate, *Chem. Eng.* 85 (41) 81 (1978).

and unleavened bread are both mentioned in the Bible. Some form of yeast or ferment acting on the carbohydrates in flour, giving CO_2 and an alcohol, was the first leavening agent used. Later, baking soda (sodium bicarbonate) was widely employed but, because it often imparted an unpleasant taste or even a yellowish color due to the alkalinity of the Na_2CO_3 formed, the search for better reagents continued. Baking powders consist of a dry mixture of sodium bicarbonate with one or more chemicals capable of completely decomposing it. The principal "baking acids" used are monocalcium phosphate monohydrate, anhydrous monocalcium phosphate, sodium acid pyrophosphate, sodium aluminum sulfate, tartaric acid, and acid tartrates. Monocalcium phosphates are consumed more than all the others, an estimate being more than 3.6×10^6 kg annually in the United States. A filler or drying agent, such as starch or flour, is usually added to the active ingredients to give a better distribution throughout the dough and to act as a diluent or to prevent the reaction until water and heat are applied. The following equations represent the actions of different baking powders:

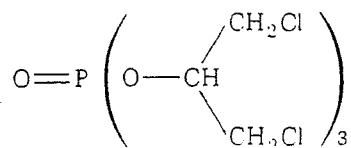


Baking powders must yield not less than 12% available CO_2 , and most powders contain from 26 to 29% NaHCO_3 and enough of the acid ingredients to decompose the bicarbonate and yield from 14 to 15% CO_2 . The rest, 20 to 40%, consists of corn starch or flour.

FIRE RETARDANT CHEMICALS

In recent years, there has been a great increase in the use of fire retardants both in flame-proofing various textiles, polymeric foams, and for combating forest fires.¹⁹ In 1971 the federal government required the use of flame retardant-treated textiles for the production of children's sleepwear, carpets, rugs, mattresses, and mattress pads.²⁰ A flame retardant enables material to resist burning when exposed to a relatively low-energy ignition source such as a cigarette, match, candle, or stove burner.

After 1971 most of the polyester sleepwear for children was made from fabrics treated with tris(2,3 dibromopropyl) phosphate, commonly known as Tris, and tris (dichloroisopropyl) phosphate, Fyrol FR-2.



Fyrol FR-2

¹⁹Lyons, *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, 1970.

²⁰Flammability, *Chem. Eng. News* 56 (17) 22 (1978).

Diethyl N,N-bis (hydroxy) ethylaminomethyl phosphonate (Fyrol 6) is used for the flame-proofing of rigid polyurethane foams. For flexible polyurethane foams, Phosgard 2XC20, 2,2-bis (chloromethyl)-1,3 propanediol-[bis(chloroethyl)] phosphate, and Fyrol FR-2 offer excellent flame retardation.

The Consumers Product Safety Commission, acting under the Federal Hazardous Substances Act, banned the use of Tris for children's sleepwear in 1977 because some tests had shown that Tris was mutagenic to bacteria, caused kidney cancer in mice and rats, and possibly was carcinogenic to humans. The use of Fyrol FR-2 for this purpose was also adversely affected although this compound had not been shown to be harmful. Large quantities of both compounds are still used for carpets and mattresses.

For combating forest and brush fires, mixtures based on $(\text{NH}_4)_2\text{HPO}_4$ or $(\text{NH}_4)_2\text{SO}_4$, thickening agents, coloring matter, and corrosion inhibitors are most commonly used. It is believed that the phosphorus compounds act as catalysts to produce noncombustible gas and char. Furthermore, phosphorus compounds which can yield phosphoric acid from thermal degradation are effective in suppressing glow reactions.²¹

SELECTED REFERENCES

- Allcock, H. R.: *Phosphorus-Nitrogen Compounds*, Academic, New York, 1972.
- Corbridge, D. E. C.: *Phosphorus*, Elsevier, New York, 1980.
- Emsley, J. and D. Hall: *The Chemistry of Phosphorus*, Wiley, New York, 1976.
- Goldwhite, H.: *Introduction to Phosphorus Chemistry*, Cambridge Univ. Press, New York, 1981.
- Johnson, J. C.: *Antioxidants* 1975, Noyes, Park Ridge, N.J., 1975.
- Martin, I. F.: *New Fire Extinguishing Compounds*, Noyes, Park Ridge, N.J., 1972.
- Porter, K. S.: *Nitrogen and Phosphorus*, Ann Arbor Sci. Publ., Ann Arbor, Mich., 1975.
- Slack, A. V.: *Phosphoric Acid*, Marcel Dekker, New York, 1968.
- Toy, A. D. F.: *Phosphorus Chemistry in Everyday Living*, ACS, Columbus, Ohio, 1976.
- TVA Fertilizer Conference, Oct. 1981, Bull. Y-170, TVA/OACD 82/5, Dec. 1981.

²¹Lowden et al., *Chemicals for Forest Fire Fighting*, National Fire Protection Association, Boston, Mass. 1963; *User Guide, Phoscheck Fire Retardant*, Monsanto Co., St. Louis, Mo., 1968.

Chapter 2

Potassium Industries

HISTORICAL. The word potash comes from the fact that extraction of wood ashes with water produces a KOH-K₂CO₃ solution. Plants selectively remove potassium from soil, acting as potash concentrators and denuding the soil of potassium, which must be replaced if the vegetation is not allowed to decay in the field and thus return potassium to the soil. Early users confused sodium and potassium hydroxides and carbonates, calling them all lye. The German Stassfurt deposits supplied the United States and most of the world with potassium salts from 1869 until World War I. When German supplies were cut off, the price of crude potassium salts rose to \$550 per metric ton of 50% muriate (KCl). U.S. production rose from 1000 t (measured as K₂O) of potash in 1915 to 41,500 t in 1919.¹ When the end of the war came, imports were resumed and production fell. Since that time, the discovery of vast new deposits has caused an increase in the amount and quality of potash salts produced. The American deposits are mined mechanically and brought to surface refineries. Solution mining of underground salines promises a lower cost procedure.^{1a} Table 2.1 shows statistics concerning potassium salt production. In 1941 and 1942 the United States produced its entire requirement of potash for the first time, and the domestic industry has continued to grow. In 1962, the International Minerals and Chemical Corp. struck rich deposits of potash in Saskatchewan, Canada.² Other companies also developed Canadian deposits into major sources of potash.³ Canadian production is over 3 times U.S. production with the U.S.S.R. producing roughly the same amount as Canada. Canadian production is almost exclusively KCl; U.S. production includes much K₂SO₄. As a consequence, although the U.S. has imported over half its requirements since 1971 (77 percent in 1980), there is a brisk U.S. export business in potassium salts.

Potassium salts are preferred over sodium salts for laboratory and pyrotechnic work because they are less hygroscopic, form fewer and simpler hydrates, and the hydrates formed are more stable to heat. For industrial purposes, these values rarely offset the substantial additional cost.

POTASSIUM

Metallic potassium was first prepared by H. Davy in 1807 by electrolysis of fused KOH. It is similar to sodium but more reactive. It is not widely used. Commercially it is not prepared

¹t = 1000 kg.

^{1a}Piombino, *Chem. Week* 93 (11; 78 (1963); Potash Minerals, *Chem. Eng. Prog.* 60 (10) 19 (1964).

²Canadian Potash Heads for Market, *Chem. Week* 90 (25) 31 (1962); Potash: a Little Tight Now, Ample by 1983, *Chem. Week* 127 (26) 28 (1980).

³Minerals Yearbook, vol. 1, U.S. Bureau of Mines, 1980.

Table 2.1 Statistics on Potassium Salts (in thousands of metric tons and thousands of dollars)

	1970	1976	1978	1979	1980	1981
United States						
Production of K salts	4,412	4,016	4,326	4,271	4,315	4,153
K ₂ O equivalent	2,481	2,177	2,253	2,225	2,239	2,159
Sales of K salts by producers	4,855	4,184	4,358	4,549	4,265	3,670
K ₂ O equivalent	2,426	2,268	2,307	2,388	2,217	1,908
Value at plant, \$	92,373	210,800	226,500	279,200	353,900	328,900
Average value, per metric ton, \$	21.60	50.37	51.97	61.38	82.98	89.62
Exports of K salts°	878	1,514	1,431	1,119	1,584	887
K ₂ O equivalent°	495	857	809	635	840	491
Value, \$	28,473	91,900	88,600	79,500	179,830	107,950
Imports of K salts for use	3,569	6,875	7,762	8,505	8,193	7,903
K ₂ O equivalent°	2,368	4,168	4,707	5,165	4,972	4,796
Customs value, \$	60,703	344,000	399,000	520,800	648,000	750,400
Apparent consumption of K salts	7,400	9,544	10,689	11,935	10,874	10,686
K ₂ O equivalent	4,300	5,578	6,205	6,918	6,349	6,213
World						
Prod'n., marketable, K ₂ O equivalent	18,194	24,281	26,113	25,677	27,673	27,357

°Excludes potassium chemicals and mixed fertilizers.

SOURCE: *Minerals Yearbook 1981*, Dept. of the Interior.

by electrolysis of fused KCl because K attacks the electrodes and tends to remain dispersed in the fused salt. Instead it is prepared from KCl by double decomposition with sodium:⁴



It is used in the high-temperature heat transfer alloy "NaK" and for the manufacture of KO₂, the dioxide used in life-support systems. It must be stored under an unreactive gas such as nitrogen.

RAW MATERIALS. The largest domestic production of potassium salts has come from deep Permian sedimentary deposits of sylvinitite [a natural mixture of sylvite (KCl) and halite (NaCl)] and langbeinite (K₂SO₄·2MgSO₄) near Carlsbad, N.Mex. The sylvinitite is mined and treated to yield high-grade potassium chloride, and langbeinite is processed to make potassium sulfate. Another domestic source of potassium salts is Searles Lake at Trona, Calif., which is a deposit of solid sodium salts permeated by a saturated complex brine. This brine is processed to separate high-grade potassium chloride and borax, together with numerous other saline products (Figs. 2.1 to 2.4). Deposits of KCl at Moab, Utah, are being solution

⁴Jackson and Werner, U.S. Patent 2,480,655 (1949).

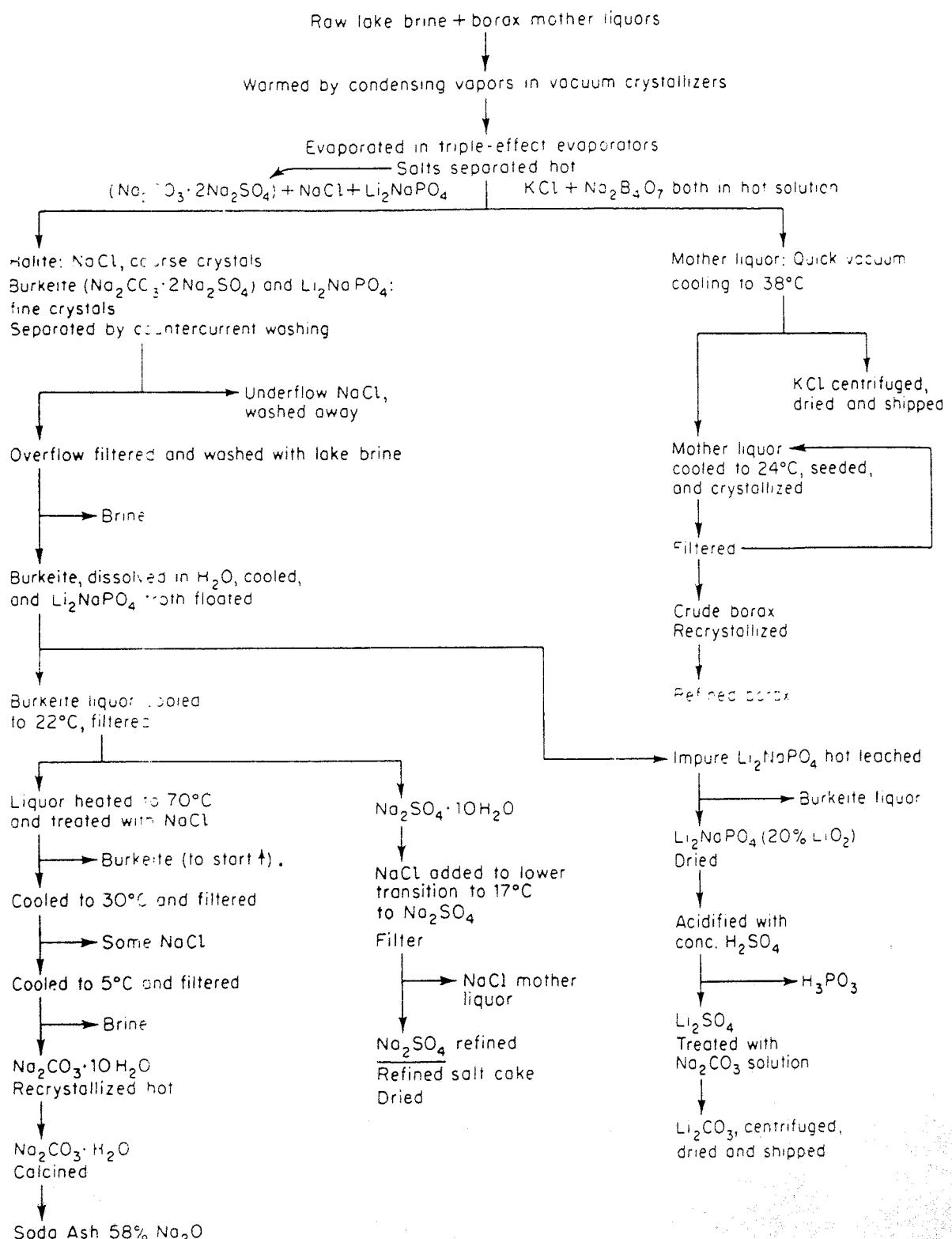


Fig. 2.1. Outline of Trona procedures. (See Chap. 20, Boron Compounds.)

mined. Great Salt Lake brines are being treated by solar evaporation to produce K_2SO_4 along with other minerals, but the project is encountering difficulties. Worldwide, currently 79 percent of all potassium salt production⁵ is KCl and 9 percent K_2SO_4 . In the United States, New Mexico mines produced 74 percent of total production, mostly K_2SO_4 (1980). Worldwide,

⁵Minerals Yearbook, vol. 1, U.S. Bureau of Mines, 1980.

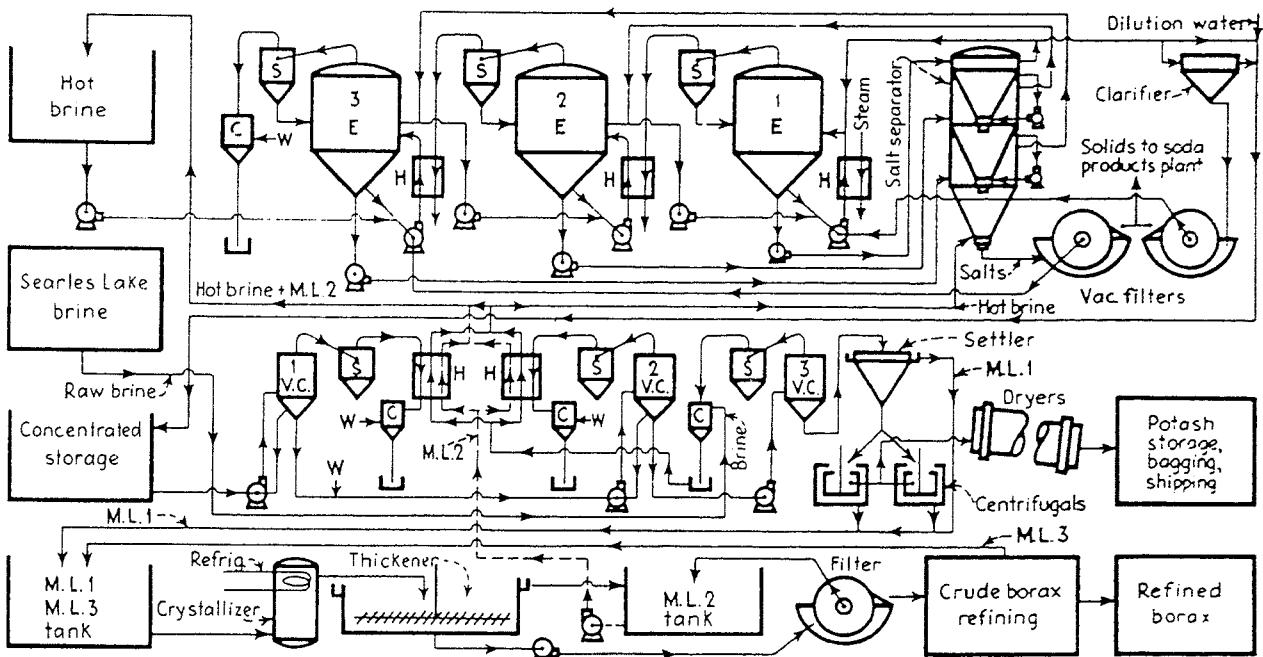


Fig. 2.2. Potassium chloride and borax by the Trona procedure. (See Fig. 17.1 for supplementary details.) Key: C, barometric condenser; E, evaporator; H, heater or heat exchanger; M.L., mother liquor; S, separator; V.C., vacuum crystallizer; W, cooling or dilution water.

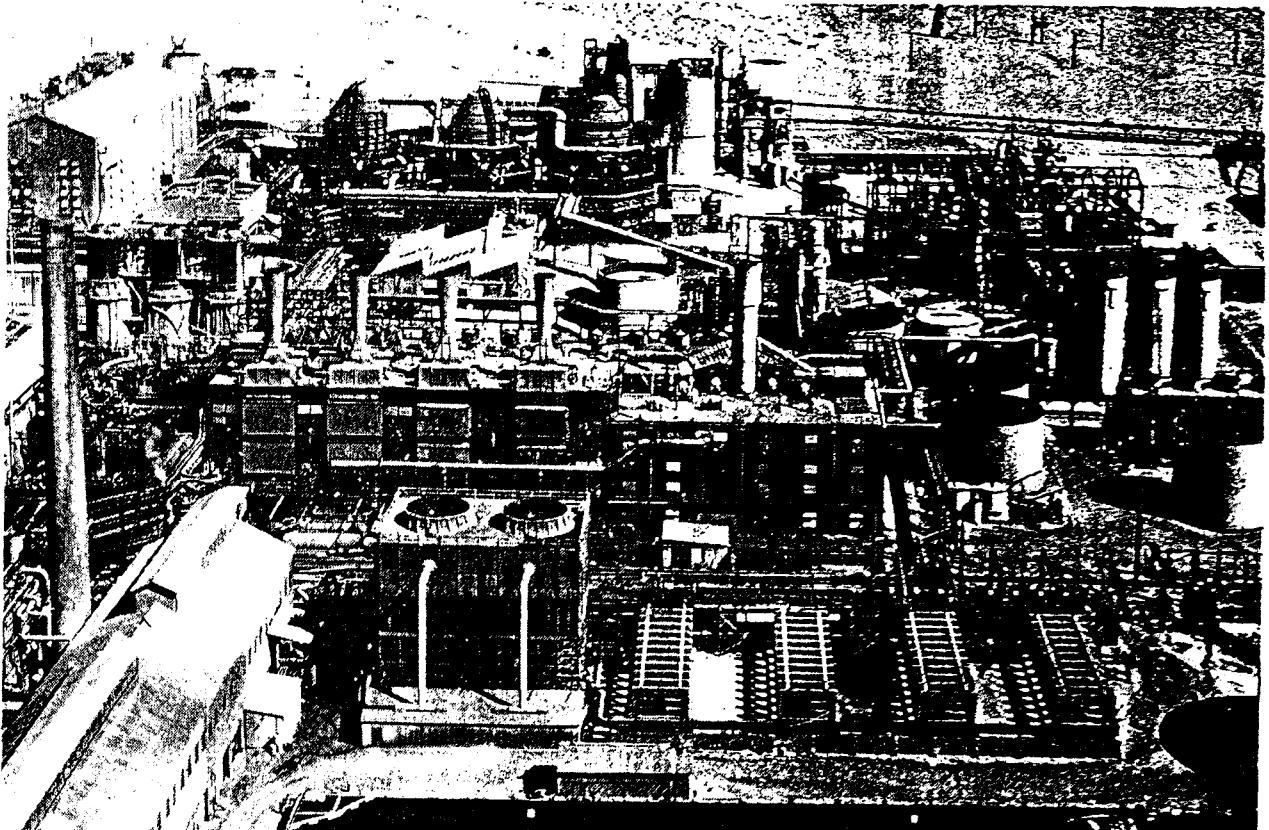


Fig. 2.3. Trona: overall view of the plant with large evaporators in the back. (American Potash & Chemical Corp.)

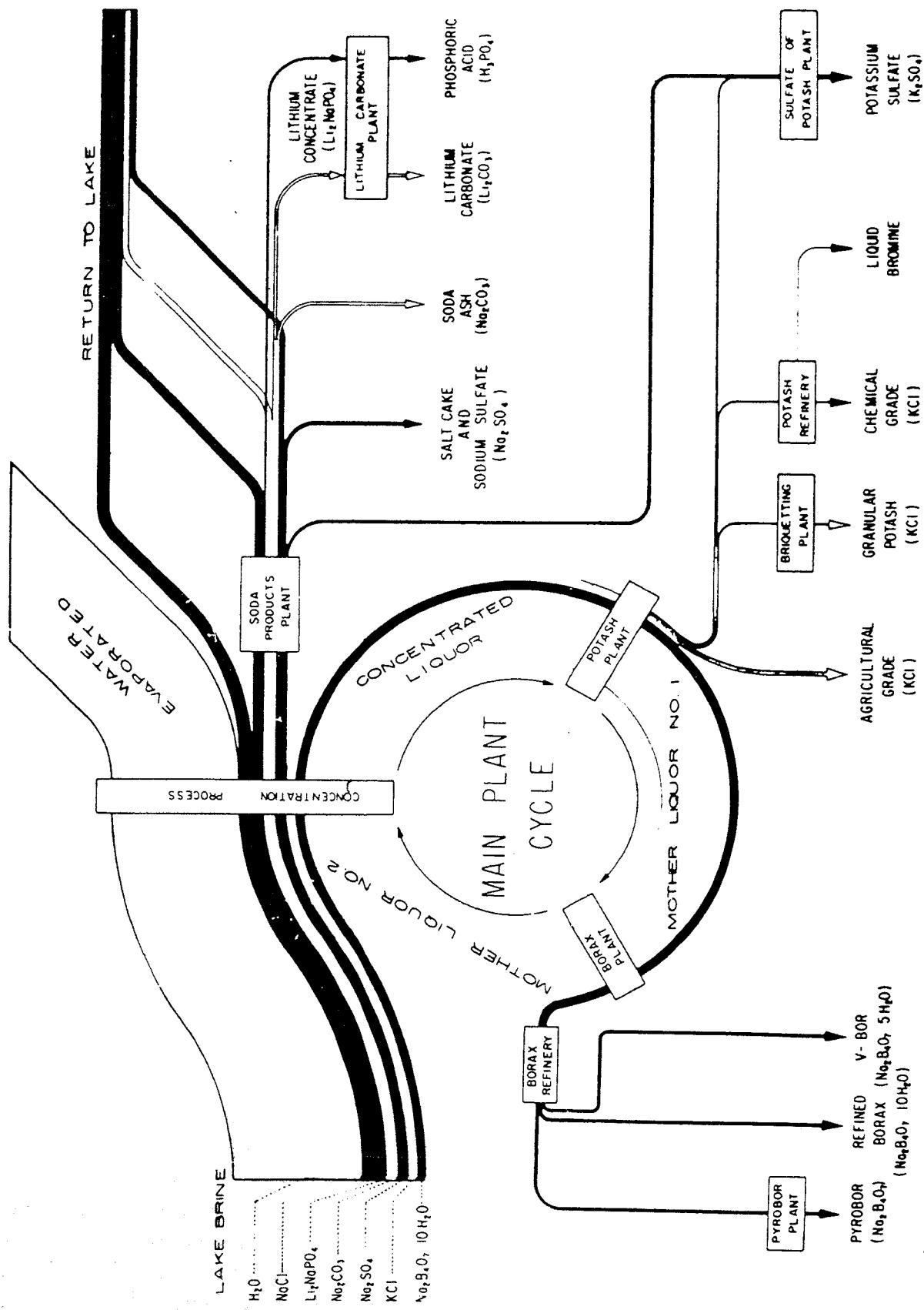


Fig. 2 .4. Trona procedures: flow of brines and salts to products. (American Potash & Chemical Corp.)

major producers are (parentheses show millions of metric tons of K₂O produced): U.S.S.R. (7.6), Canada (7.3), East Germany (3.2), West Germany (2.3), United States (2.2), France (1.8), and others (1.7). Israel and Jordan are building plants on the Dead Sea which are expected to have large capacities. Brazil and China also are producers of increasing quantities. Since sodium and potassium are of about equal abundance in the earth's crust, the distribution of potassium salt deposits is wide. It is strange that the seas contain so little potassium; this is accounted for by the great affinity of both soil and plants for potassium compounds.

POTASSIUM CHLORIDE

In this country about 90 percent of the potassium chloride is produced as fertilizer grade of about 97% purity. In the fertilizer trade it is referred to as *muriate of potash*. The chemical grade, or 99.9% potassium chloride, is the basis of the manufacture of most potassium salts.

MANUFACTURE BY THE TRONA PROCESS. From Searles Lake, Calif., the shipping of potash was begun in 1916 and, including numerous other products, has continued since that time on an ever-expanding scale. The lake is composed of four layers. The upper layer of crystalline salt is from 20 to 30 m deep; the second layer, about 4 to 5 m of mud; the third layer, about 8 m of salt; and the bottom layer is mud interspersed with minor salt seams. In processing, the brine is pumped from the interstices in the salt body from the first and third layers. The brines have the following approximate constant composition:

Expressed As	Upper Deposit, %	Lower Deposit, %
KCl	4.85	3.00
NaCl	16.25	16.25
Na ₂ SO ₄	7.20	6.75
Na ₂ CO ₃	4.65	6.35
Na ₂ B ₄ O ₇	1.50	1.77
Na ₃ PO ₄	0.155	
NaBr	0.109	
Miscellaneous	0.116	0.35
Total salts (approx.)	34.83	34.60
H ₂ O	65.17	65.40
Specific gravity	1.303	1.305
pH (approx.)	9.45	9.60

As determination of the composition of the various salts from the German potash deposits at Stassfurt by van't Hoff from 1895 to 1910 helped greatly in the development of the German potash industry, likewise the phase-rule study⁶ of the much more complex systems existing at

⁶Teeple, *Industrial Development of Searles Lake Brines*, Reinhold, New York, 1929; Robertson, The Trona Enterprise, *Ind. Eng. Chem.* 21 520 (1929); Expansion of the Trona Enterprise, *Ind. Eng. Chem.* 34 133 (1942); Gale, Chemistry of the Trona Process from the Standpoint of the Phase Rule, *Ind. Eng. Chem.* 30 867 (1938). The triangular phase diagrams of the more common constituents of Searles Lake brine at 20 and 100°C are presented and described in Kobe, *Inorganic Chemical Processes*, Macmillan, New York, 1948, pp. 71-74ff. These are for the brines saturated with NaCl at all points and for burkeite, Na₂SO₄, glaserite, KCl, and Na₂CO₃.

Searles Lake by Morse, Teeple, Burke, Mumford, Gale, and many others was another striking investigation carried to successful application in the Trona process. In the first-layer brine of Searles Lake the main system is $\text{Na}-\text{K}-\text{H}-\text{SO}_4-\text{CO}_3-\text{B}_2\text{O}_4-\text{Cl}-\text{F}-\text{H}_2\text{O}$. The references cited, particularly the one by Gale, demonstrate with appropriate solubility charts this important and commercial application of the phase rule, wherein the conditions are presented for the desired fractional crystallization.

The chemists and engineers at Trona have been ingenious in obtaining pure salts from this complex brine and in building a profitable industry in a competitive field and under the handicap of being in the desert 320 km from the nearest major city. The town of Trona, Calif., houses more than 2000 inhabitants dependent on this one industry. Figure 2.1 outlines the steps, based on the phase-rule study, necessary to commercialize this brine. Figure 2.2 gives more details of the division of the procedures leading to potassium chloride, borax, and soda products. There is no profitable market for the large tonnages of common salt obtained, and it is washed back into the lake.

In general, this successful process is founded upon many years of intensive research wherein exact conditions were worked out and then applied in the plant. In barest outline this involves the concentration of potassium chloride and borax in hot brine and the simultaneous separation of salt and burkeite, a new mineral with the composition $\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$. By virtue of the delayed crystallization of borax, potassium chloride can be obtained by rapid cooling of the concentrated brine in vacuum coolers and crystallizers.⁷ After centrifugation, the potash mother liquor is refrigerated and furnishes borax.

The somewhat detailed⁸ flowchart in Fig. 17.2 can be resolved into the sequences that follow.

Concentration and soda-products separation

Raw brine is mixed with end liquors from the borax crystallizing house and pumped into the third effect of triple-effect evaporators.

The brine is hot-concentrated, and salted out in the three effects counter to the steam flow (Figs. 2.3 and 2.4).

The suspended salts, NaCl and $\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$, are removed from the liquors of each effect by continuously circulating the hot liquor through cone settlers called *salt separators*, or *salt traps*. The underflow from the first-effect cone containing the salts passes through an orifice into the second-effect cone, receiving a countercurrent wash with clarified liquor from the second-effect cone. The combined salts from the first and second cones are given a countercurrent wash with liquor from the third cone as they pass through an orifice into their third cone. The combined salts of the first, second, and third cones receive a countercurrent wash with raw brine as they leave the third-effect cone. All these are hot washes. The combined underflow is filtered, and the filtrate returned to the evaporators.

⁷Perry, 5th ed., pp 17-8 to 17-19; Turrentine, *Potash in North America*, Reinhold, New York, 1943. (The first vacuum cooler-crystallizer is pictured and described.) Turrentine's invention has had a profound influence upon the cheap production of pure potassium chloride both in the United States and abroad.

⁸Mumford, Potassium Chloride from the Brine of Searles Lake, *Ind. Eng. Chem.* 30 872 (1938); Kirkpatrick, A Potash Industry; at Last, *Chem. Met. Eng.* 45 488 (1938); Searles Lake Chemicals, *Chem. Met. Eng.* 52 (10) 134 (1945).

The cake (salt: NaCl and $\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$) is sent to the soda-products plant (middle lower part of Fig. 2.1).

The final hot, concentrated liquor is withdrawn from the overflow of the first-effect cone into an auxiliary settler called a clarifier. The overflow from the clarifier is pumped to storage at the potash plant.

The underflow from the clarifier is filtered and treated in the same manner as the previous underflow.⁹

Separation of potassium chloride

The hot, concentrated liquor leaving the clarifiers is saturated with potassium chloride and borax. The potassium chloride is obtained by cooling quickly to 38°C and crystallizing in three-stage vacuum cooler-crystallizers.

Enough water is added to replace that evaporated so that the sodium chloride remains in solution.

The suspension of solid potassium chloride in the mother liquor is passed to a cone settler, where the thickened sludge is obtained as the underflow.

The potassium chloride is dried in rotary driers, yielding 97% potassium chloride. This salt is conveyed to storage, to the bagging plant, or to a recrystallizing procedure.

Separation of borax¹⁰

The overflow, combined with the filtrate, is pumped to the borax plant for removal of borax.

The potash mother liquor is cooled in vacuum crystallizers as shown in Fig. 17.2. The water lost by evaporation is returned to the boiling (but cooling) solution to prevent the concentration of this solution with consequent crystallization of potassium chloride with the crude borax.

The borax crystallizes out as a crude sodium tetraborate pentahydrate.

The crude borax is filtered off and washed.

The filtrate is returned to the start of the evaporator cycle.

When necessary, the crude borax is refined by recrystallization.

This salt is centrifuged, dried, and packaged for market.

The preceding description deals with the processing of the upper brine layer. In 1948 a new plant was finished at Trona for the lower brine layer. The process used involves carbonation of this brine with flue gas from the boiler plant.¹¹ The sodium bicarbonate separated by this reaction is calcined and converted to dense soda ash. Crude borax is crystallized from the carbonated end liquor by cooling under vacuum, and the filtrate is returned to the lake. The daily production of American Potash and Chemical Co. is approximately 525 t of muriate of potash, with borax, boric acid, salt cake, and soda ash as coproducts. Evaporation is at the rate of several million kilograms of water per day. To effect the requisite heat transfer when

⁹Mumford, op. cit., pp. 876, 877; Hightower, The Trona Process, *Chem. Eng.* 58 (8) 104 (1951) (excellent flowcharts).

¹⁰See Chap. 20 for boron compounds for the solvent extraction of boric acid from Searles Lake brine and from borax mother liquors.

¹¹Hightower, New Carbonation Technique: More Natural Soda Ash, *Chem. Eng.* 58 (5) 162 (1951); 56 (4) 102 (1949).

salts crystallize out at the same time was a major chemical engineering problem. This problem was solved by removing the piping from inside the evaporators and doing the heating in outside heaters under mild hydrostatic pressure with minimum evaporation.¹² The superheated solution is flashed into evaporators. Heat transfer is also facilitated by vacuum cooling through vaporization instead of using cooling liquids in coils, which would become fouled with encrusted solids. The increased cost of energy has resulted in careful analysis of the processes and led to substantial reduction in energy use, but the actual changes made have not yet been disclosed.

The extraction of *soda and lithium products*¹³ is a development resulting from an extension of the phase studies. Figure 2.1 outlines the production of soda ash, anhydrous sodium sulfate, and lithium carbonate. Figure 2.4 diagrams the flow of brines and salts at Trona.

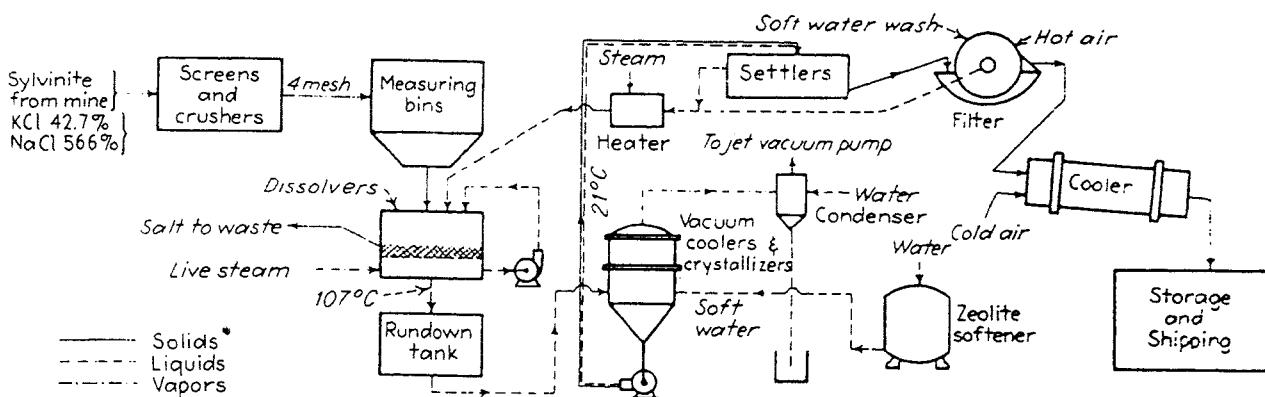
MANUFACTURE FROM SYLVINITE. In 1925 potash was discovered at Carlsbad, N.Mex.¹⁴ After much prospecting and drilling, a shaft to mine the mineral was sunk to about 300 m. and in 1932 a refinery was constructed.

The process employed by the United States Borax and Chemical Corp. depends primarily upon the fact that sodium chloride is less soluble in a hot than in a cold saturated solution of potassium chloride. Thus, when a saturated solution of the mixed salts in water is cooled from its boiling point, potassium chloride separates out, contaminated with only the sodium chloride that is entrained. The cold mother liquor is heated to 110°C by the use of heat exchangers employing exhaust steam, as shown in Fig. 2.5. The hot mother liquor is passed through a series of steam-heated turbomixer dissolvers countercurrent to a flow of ore crushed to -4 mesh size, which is moved from dissolver to dissolver by mechanical elevating equipment. The potassium chloride goes into solution, together with a small amount of sodium chloride. In this step colloidal and semicolloidai clays present in the ore are suspended in the potash-bearing solution. The enriched mother liquor passes through thickener equipment, where this insoluble mud settles out. The underflow mud is washed by countercurrent decantation in a tray thickener, and the not-clear, saturated overflow solution is pumped to vacuum coolers and crystallizers. Tailings from this process, largely sodium chloride, after passing through Bird centrifuges where adhering potash-bearing brine is removed, are carried out of the plant to waste storage. Vacuum in the coolers and crystallizers is maintained by means of steam ejectors. In these vessels the solution is cooled to 27°C, and the potassium chloride comes out of solution and, in suspension, is pumped to settling tanks where a large part of

¹²Manning, Capital + Vision + Research = An American Potash Industry, *Chem. Met. Eng.* 36 268 (1929).

¹³Reburn and Gale, The System Lithium Oxide-Boric Oxide-Water, *J. Phys. Chem.* 57 19 (1955); Robertson, Expansion of the Trona Enterprise, *Ind. Eng. Chem.* 34 133 (1932); Gale, Lithium from Searles Lake, *Chem. Ind.* 57 422 (1945); Salt Lake Projects, *Chem. Eng. News* 46 (16) 11 (1968); Potash, *Chem. Week* 105 (21) 36 (1969).

¹⁴Smith, Potash in the Permian Salt Basin, *Ind. Eng. Chem.* 30 854 (1938). For the separation of two salts with a common ion, like NaCl-KCl, see the phase diagrams figs. 3-1 and 3-2 of Kobe, *Inorganic Process Industries*, Macmillan, New York, 1948; Ullmann, *Enzyklopädie der technischen Chemie*, vol. 9, 1957, p. 187 (phase diagrams and flow diagrams); Gaska et al., Ammonia as a Solvent (to prepare pure KCl from NaCl, KCl), *Chem. Eng. Prog.* 61 (1) 139 (1965).



In order to produce 1 t of refined KCl, the following materials and utilities are required:

Sylvinite	2.51 t	Electricity	180 MJ
Water	170–200 m ³	Direct labor	4–5 work-h
Steam	1250 kg		

Fig. 2.5. Potassium chloride (muriate) from sylvinite, with continuous flow dissolving for hot-solution refining. (U.S. Potash Corp.)

the liquor is decanted through launders to be used again. The thickened crystal mass is filtered, washed, and dried on Oliver filters. The dried cake is crushed, screened, and conveyed either to a warehouse or to cars.

A plant for producing granular 50% potassium chloride, used almost entirely by the fertilizer industry, operates as follows. Crushed and sized ore suspended in a brine saturated with both sodium and potassium chloride is carried to a bank of Wilfley tables, where sodium chloride and potassium chloride are separated by their difference in gravity. A product carrying 50 to 51% K₂O is debrined in drag classifiers and passed through gas-fired rotary dryers, from which it goes to storage and shipping. A middling product is further tabled after debrining, and the tailing is debrined and carried to a salt-storage pile.

The process of the Potash Company of America separates potassium chloride from sodium chloride chiefly by a metallurgical concentration method using a *soap-flotation* process and represents the first adaptation to water-soluble ores of the flotation principle so long familiar in the concentration of insoluble ores. The sylvinite ore, having been coarsely crushed underground, is fed to an intermediate crusher, which in turn discharges to fine crushers. The ore is then wet-ground by ball mills to 100 mesh. The mill product is treated in two series of flotation cells to float off an NaCl concentrate and depress a KCl concentrate. The NaCl crystals are washed and separated from the solution by means of a thickener and a filter and sent to waste while the KCl concentrate, together with KCl crystals recovered from various circulating solutions, is separated by a classifier into fine and coarse fractions. Recovery of fines is accomplished by a thickener and centrifuges.

The *flotation* process is used also by International Minerals and Chemical Corp. in the refining of sylvinite to produce potassium chloride. This company also processes potassium sulfate from the mineral langbeinit (K₂SO₄ · 2MgSO₄) by reacting it with potassium chloride to yield the sulfate and the by-product magnesium chloride. The latter is of particular interest as a raw material for the production of metallic magnesium, potassium chloride, and sulfate of potash-magnesia. Great Salt Lake minerals have also been separated by a flotation process¹⁵

¹⁵Tippin, Potash Flotation Method Handles Variable Feed, *Chem. Eng.* 84 (15) 73 (1977).

using an anionic short-chain, saturated fatty acid collector to float schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$).

POTASH FROM SASKATCHEWAN, CANADA. This is North America's major source of supply. It is estimated that it will satisfy the world potash demand for more than 600 years. It is, however, deep down—1100 or more meters—and layers of water-soaked deposits and quicksand must be penetrated. This was accomplished by the International Minerals and Chemical Corp.¹⁶ It proved to be America's toughest mining venture and involved solidifying 90 m of the prospective 6-m-diameter shaft area by refrigeration with lithium chloride brine. About 1½ years was required to freeze through the 61 m of quicksand, after which the shaft was dug and then lined with cast-iron circular segments at a cost of \$2 million. The installation of hoisting machinery followed.

The refinery for processing the raw salts from the mine has been operating¹⁷ since 1963. The ore is sylvinit (xNaCl·KCl) and carnallite (KCl·MgCl₂·6H₂O) (Fig. 2.6). The International Minerals and Chemical Corp. process as depicted grinds and sizes the ore. This ore is treated with a brine which leaches out the carnallite, deslimes the ore, and then separates the potassium salts into fines and coarse material. After this separation, the fines are deslimed by a hydroseparator, treated with an amine and starch, and combined with the coarse salts, which are similarly treated. Both the fines and the coarse salts are conducted to flotation cells to separate the potassium salts from the sodium chloride by flotation. When the ore is treated with the brine, the carnallite is decomposed, dissolving the magnesium chloride, and the potassium chloride begins to crystallize. Fresh water added continuously prevents the brine from becoming saturated with magnesium chloride. Although some potassium chloride dissolves, the main brine effluent carries mostly sodium chloride and potassium chloride.

Fertilizer Use. Over 90 percent of potash salts mined enter the fertilizer field, mostly as mixed fertilizers. These are presented in Chap. 26 on agrichemicals.

POTASSIUM SULFATE

Prior to 1939, the German potash industry was the chief source of potassium sulfate for the American chemical and fertilizer industries, although considerable tonnages were being produced in this country by the interaction of potassium chloride and sulfuric acid as a coproduct of salt-cake manufacture. With the termination of European imports, the production of the salt was undertaken on a larger scale by the American Potash and Chemical Corp. through the interaction of burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) with potassium chloride, followed in turn by the successful recovery of this salt from langbeinite by the International Minerals and Chemical Corp. In agricultural use potassium sulfate is preferred for the tobacco crop of the southeast and the citrus crop of southern California.

¹⁶Potash Industry, *Chem. Eng. News* 46 (38) 20 (1968); Potash, *Chem. Week* 127 (26) 28 (1980).

¹⁷Cross, World's Largest Supply Feeds New Potash Plant, *Chem. Eng.* 69 (23) 176 (1962) (flowchart, pictures, description); Gaska et al., Ammonia as a Solvent (for NaCl, KCl), *Chem. Eng. Prog.* 61 (1) 139 (1965)

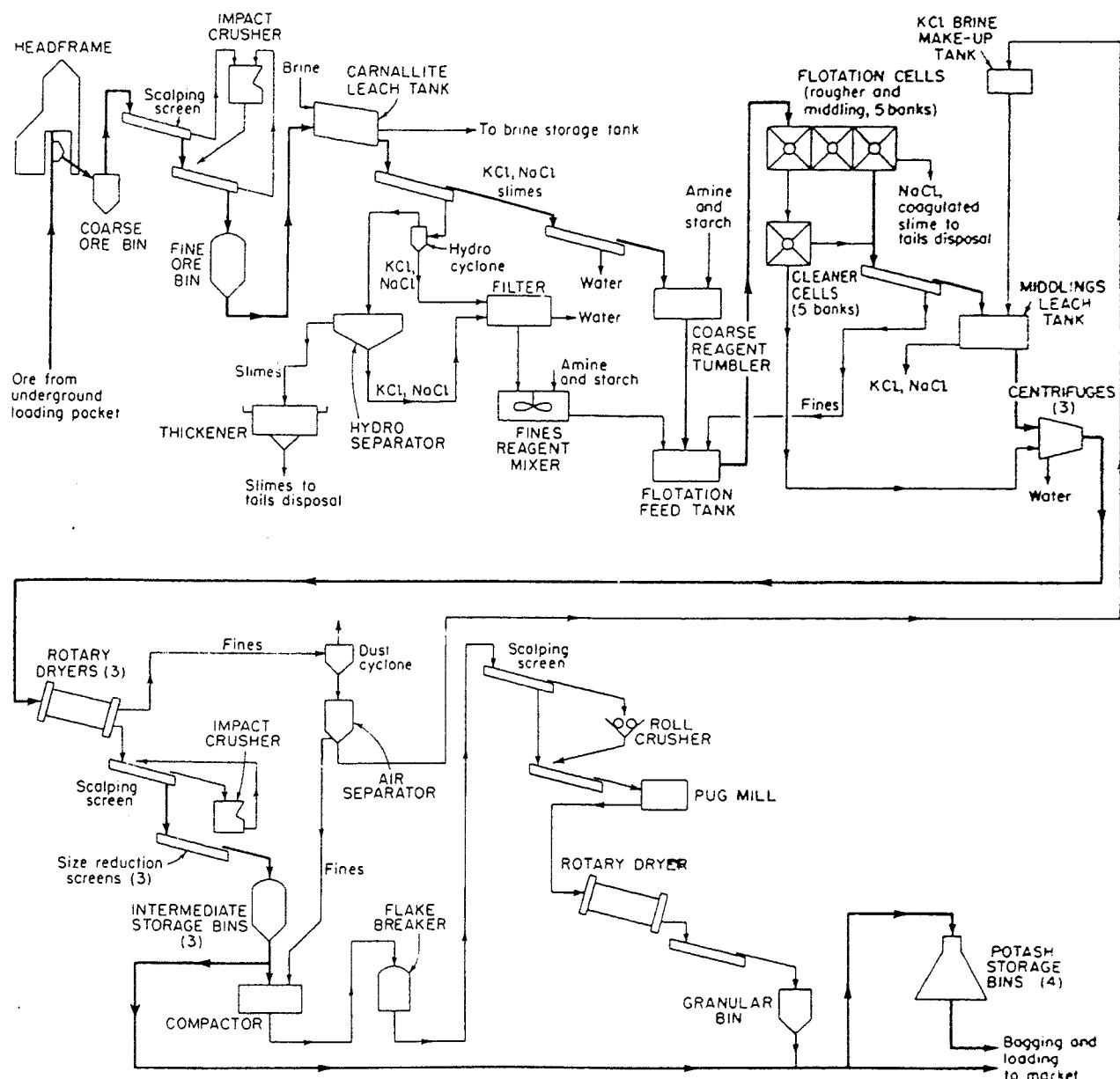


Fig. 2.6. Potash mine and refinery. Banks of flotation cells separate potash particles from NaCl. [International Minerals & Chemical Co., Esterhazy, Saskatchewan, Canada; Chem. Eng. 68 (23) 176 (1962).]

POTASSIUM BISULFATE

Potassium bisulfate is readily prepared from K_2SO_4 by reaction with sulfuric acid. It is a strongly acidic material and is used as a flux for ceramics.

POTASSIUM HYDROXIDE

Potassium hydroxide (caustic potash) is made by the electrolysis of KCl using procedures similar to those for NaOH. Some electrolytic plants shift back and forth between KOH and

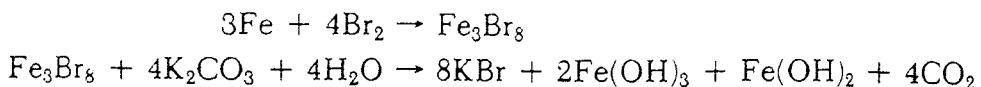
NaOH to meet market demands. Five U.S. producers made 357,000 t in 1981. Of this, 25 percent was converted to potassium carbonate, 17 percent used to make liquid fertilizers, 10 percent reacted to form potassium phosphates, and 6 percent used for potassium permanganate; the rest went into pesticides and other chemicals.

POTASSIUM CARBONATE

Potassium carbonate (pearl ash) is made by reacting caustic potash with carbon dioxide. This is the preferred source of potash for hard glass. It is also used for making pottery, smalts, and soaps; for engraving processes; for finishing leather; and as an absorbent for acid gases (CO₂ and H₂S).

POTASSIUM BROMIDE

Potassium bromide is the classical sedative, but now its greatest use is in photographic emulsions and photoengraving. It is made by first forming iron bromide by the reaction of liquid bromine and scrap iron (usually stampings or borings). This is then reacted with K₂CO₃ (sometimes KOH) to form the salt, which is filtered and crystallized.

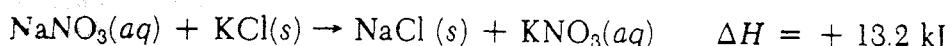


POTASSIUM IODIDE

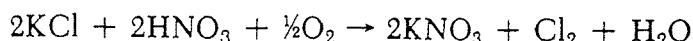
Potassium iodide is made in essentially the same way as KBr, except that iodine is used to dissolve the iron. It is valuable for photographic use, in animal and human feed (particularly to make iodized salt), and in pharmaceutical preparations.

POTASSIUM NITRATE

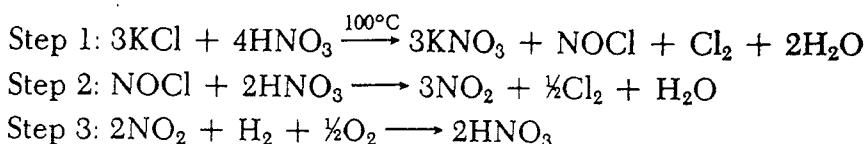
Potassium nitrate, once in great demand as a constituent of black powder, is now used more prosaically as a fertilizer, in pyrotechnic mixtures, as a heat-transfer medium (as a eutectic mixture with NaNO₂), for heat-treating steel, and in foods. Originally recovered from spots where bacterial action on human and animal manure had formed it and evaporation made it crystalline (Parisian cellars and Indian stables), it later was recovered from Chile saltpeter, which is about 10% potassium nitrate. It is now usually made by double decomposition between NaNO₃ and KCl:



A strong, hot solution of NaNO_3 is made, and solid KCl is dumped into the kettle. Upon heating, the KCl crystals change to NaCl crystals, and the hot potassium nitrate solution is run through the NaCl crystals at the bottom of the kettle. A little water is added to prevent further deposition of NaCl as the solution is cooled. A good yield of potassium nitrate results. The Southwest Potash Co.¹⁸ makes potassium nitrate at its fertilizer plant at Vicksburg, Miss., reacting KCl from the company's Carlsbad plant with nitric acid to furnish 63,000 t/year of potassium nitrate and 22,000 t of chlorine.¹⁹



The step-by-step reactions are:



The key process features are (1) a shift in the composition of the nitric acid-water azeotrope from about 70% HNO_3 to over 80% HNO_3 , in the presence of KNO_3 at high concentration, and (2) the capability of oxidizing nitrosyl chloride to Cl_2 and NO_2 with nitric acid in the 70 to 80% concentration range at temperatures and pressures that are practical for operation. Potassium nitrate made in this fashion is nearly competitive with potassium sulfate as a source of potassium and nitrogen and is preferred over KCl for plants, such as tobacco, that are adversely affected by chloride in the soil.

Black powder is no longer a military propellant but is essential as an igniter for smokeless powder and as the combustible in slow-burning fuses.

POTASSIUM ACID TARTRATE (Bitartrate)

Pomace, the fruit residue left after pressing fruits for juice, and argols, the precipitate formed in wine vats, are processed for the domestic production of potassium acid tartrate. Crude argols are also imported. Leaching and crystallization produce the commercial salt. As *cream of tartar* it is used in some types of baking powder, in medicine, and as the K, Na salt in crystals for electronic use.

POTASSIUM PERMANGANATE

Potassium permanganate can be made by passing CO_2 through a potassium manganate solution, which is made by treating MnO_2 with KOH and O_2 . This much-favored laboratory

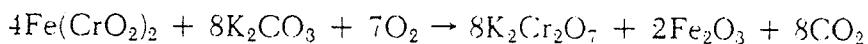
¹⁸Nitrate Potash, *Chem. Eng.* **71** (1) 44 (1964).

¹⁹Speelman, New Route to Chlorine and Saltpeter, *Chem. Eng.* **72** (23) 198 (1965) (flow-chart and details); Mehring et al., Potassium Nitrate, *Ind. Eng. Chem.* **21** 379 (1929); Synthetic Saltpeter Scores, *Chem. Week* **97** (4) 35 (1965).

reagent is far too expensive to use as a commercial oxidizing agent and is made only in small quantity.

POTASSIUM DICHROMATE

Potassium dichromate (bichromate) is another expensive oxidizing agent with a few specialized industrial uses which can usually be filled by the less expensive sodium salt. It is made by roasting caustic potash, quicklime, and chrome-iron ore:



The quicklime serves only to keep the melt porous so air can enter and react. It can also be made by reacting sodium dichromate with KCl.

SELECTED REFERENCES

American Potash Association. Publications.

Devonshire, G. S. and D. N. Maclean: The Potash Industry, *Lubrication* 54 (4) 37 (1971) (Texaco Co., New York)

Noyes, R.: *Potash and Potassium Fertilizers*, Noyes, Park Ridge, N.J., 1966.

Sauchelli, V. (ed.): *Chemistry and Technology of Fertilizers*, ACS Monograph 148, Reinhold, New York, 1960.

Chapter 3

Nitrogen Industries

Fixed nitrogen from the air is the major ingredient of fertilizers which make intensive food production possible. During the development of inexpensive nitrogen fixation processes, many principles of chemical and high-pressure processes were clarified and the field of chemical engineering emerged. Before synthetic nitrogen fixation, wastes and manures of various types, or their decomposition products, and ammonium sulfate as a by-product from the coking of coal were the primary sources of agricultural nitrogen. They were messy and insufficient to meet needs. Chilean saltpeter, saltpeter from human and animal urine, and later ammonia recovered from coke manufacture became important, then were replaced by synthetic ammonia and nitrates. Ammonia is the base from which virtually all nitrogen-containing products are derived.

HISTORICAL. Priestly and Cavendish passed electric sparks through air and produced nitrates by dissolving the oxides of nitrogen thus formed in alkalies. Commercial development of this process has proved elusive, for much electrical energy is consumed at low efficiency. Nitrogen has been fixed as calcium cyanamide, but the process is too expensive except for producing chemicals requiring the cyanamide configuration. Other processes, such as thermal processing to mixed oxides of nitrogen (NO_x), cyanide formation, aluminum nitride formation, and decomposition to ammonia, etc., show little commercial promise although they are technically possible. Haber and Nernst made careful studies of the equilibrium between nitrogen and hydrogen under pressure to form ammonia and discovered several suitable catalysts. No high-pressure apparatus was then available, and they had to invent as they went along. Haber and Bosch also worked out processes for obtaining inexpensive pure hydrogen and nitrogen by workable processes. The obvious electrolysis of water for hydrogen production and the distillation of liquid air to provide nitrogen proved unduly expensive, so they derived other, better processes. These cooperative efforts made the commercial high-pressure synthesis of ammonia possible by 1913. This energy-intensive process has undergone considerable modification in recent years, resulting in prices which have not escalated as rapidly as energy prices in general. Major improvements are very recent and are continuing at a fast pace.

USES AND ECONOMICS. Ammonia is the most important nitrogenous material. Most is made synthetically but some continues to be obtained as by-product. Chilean saltpeter (NaNO_3) continues to be mined and is a significant source of fixed nitrogen. Ammonia gas is used directly as a fertilizer, in heat treating, paper pulping, nitric acid and nitrates manufacture, nitric acid ester and nitro compound manufacture, explosives of various types, and as a refrigerant. Urea, hydroxylamine, and hydrazine are made from it. Amines, amides, and miscellaneous other organic compounds are derived from ammonia. Use of ammonia as a fertilizer is very great but remains far below that desirable for maximum crop production. Thirteen